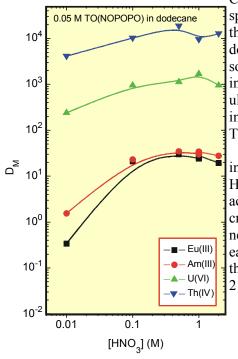
A New Extractant for Actinide Partitioning

Both the high throughput of solvent extraction and the more than 50 years of accumulated experience for processing of radioactive materials by this method ideally qualify this science and technology for solving the problems of actinide and fission product isolation, recycle, and disposal. Recently, the Chemical Separations and Coordination Chemistry group at Argonne National Lab and the research group of Professor R. T. Paine at the

University of New Mexico have begun a collaboration to develop new reagents and processes to increase the efficiency of solvent extraction-based separations for actinide recycle. Our intent is that new processes will respond to $21^{\rm st}$ Century demands for protection of the environment.

Professor Paine's group has extensively investigated for a number of years the lanthanide coordination properties of reagents based on pyridine-N-oxides substituted with one or two phosphine oxide (NOPO(PO)) ligating groups. The tetraphenyl derivatives created by the Paine group are powerful tridentate ligands for lanthanide coordination. These derivatives and their metal complexes have been characterized by X-ray crystallography and spectroscopy which has led to good understanding of their lanthanide binding properties. However, the tetraphenyl derivatives that are good for structural studies are poorly soluble in the types of solvents that might be used for large-scale separations of actinides. Consultation between our groups led to the synthesis of tetra(octyl) and tetra(2-ethylhexyl) derivatives of the same chelating agents (at right). These compounds are soluble in aliphatic hydrocarbons and thus amenable to testing for actinide partitioning.

Continuing investigations of the actinide extraction properties of both the tetraoctyl (TO(NOPOPO)) and the tetraethylhexyl (TEH(NOPOPO)) derivatives have established that the extraction efficiency of these compounds is somewhat greater than that of the well-known actinide extractant CMPO, the basis of the TRUEX process (see figure below). It also differentiates between the actinide oxidation states somewhat more significantly than does



CMPO, potentially increasing opportunities for oxidation state specific partitioning of the actinides. Our initial investigations of the thermodynamics of extraction suggest that the NOPOPO extractants do not engage in tridentate coordination of actinides in organic solutions, though they are effective reagents. We will to use this information to guide additional adjustments to the extractant and ultimately to develop viable processes based on the use of these important new reagents - perhaps creating a next-generation TRUEX process.

Our collaboration represents an exciting new avenue for increasing the impact of the fundamental science funded by the BES Heavy Elements program, as we have combined the best features of academic research and national laboratory facilities and expertise to create an opportunity for developing new solutions to pressing needs of the country. Though much work remains to be done, these early results encourage us to believe that we might be able to use this approach to close the loop on radioactive waste disposal in the 21st century.

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